Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Selective or living organopolymerization of a six-five bicyclic lactone to produce fully recyclable polyesters

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Materials and Methods

Air and moisture sensitive materials and syntheses were handled and performed in flame-dried Schlenk-type glassware on a dual-manifold Schlenk line or in an N_2-filled glovebox. High-performance liquid chromatography (HPLC)-grade organic solvents were first sparged extensively with nitrogen during filling of 20 L solvent reservoirs and then dried by passage through activated alumina (for THF), followed by passage through Q-5 supported copper catalyst stainless steel columns (for toluene). THF was further dried by stirring over sodium-potassium alloy for 24 h at room temperature followed by filtration and distillation under N_2; toluene was further dried by stirring with flame-activated CaH_2 for 24 hours followed by distillation under N_2. Anhydrous ethanol (Pharmco Aaper) was used as received and stored over activated 3Å molecular sieves. Benzyl alcohol (Sigma Aldrich), $CDCl_3$ (Cambridge Isotope Laboratories), and aniline (Alfa Aesar) were dried and distilled over CaH_2 before use. Thiourea and urea catalysts were synthesized and purified according to literature procedure;[1] cyclohexylamine (Alfa Aesar), phenylisocyanate (Beantown Chemical), phenylisothiocyanate (TCI), 3,5-bis(trifluoromethyl)phenyl isocyanate (TCI), 3,5-bis(trifluoromethyl)phenyl isothiocyanate (TCI), 3,5-bis(trifluoromethyl)aniline (Alfa Aesar), and 1,3-diisopropyl thiourea (Sigma Aldrich) were used as received, and 1,3-diphenyl urea (TCI) was recrystallized from ethyl acetate before use. NHC 1,3-isopropylimidazol-2-ylidene (I^iPr) was synthesized according to literature procedure.[2] L-Lactide (Sigma Aldrich) was purified by sublimation. Cyclohexene oxide (TCI), diethyl malonate (Beantown Chemical), sodium ethoxide (Beantown Chemical), potassium hydroxide (Fisher), 1,3-dimesitylimidazol-2-ylidene (IMes, TCI), 1,3-di-*tert*-butylimidazol-2-ylidene (I^tBu, TCI), 2-tert-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP, Sigma Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Beantown Chemical), and potassium methoxide (KOMe 95%, Sigma Aldrich) were used as received.

Preparation of Monomer 4,5-T6GBL

The literature procedure[3] was modified for the preparation of 4,5-T6GBL. To a 1 L, 3-neck flask equipped with a stir bar, addition funnel, and reflux condenser was added 14.8 g (21.8 mmol, 1.09 equiv.) sodium ethoxide and 160 mL anhydrous ethanol under a nitrogen atmosphere. The mixture was stirred vigorously for 1 h to completely dissolve ethoxide. Diethyl malonate (31.9 mL, 21.0 mmol, 1.05 equiv.) was added to the addition funnel via syringe, dripped into the reaction flask over 30 min and stirred another 90 min to ensure complete enolate formation. Cyclohexene oxide (20.2 mL, 20 mmol, 1 equiv.) was then added to the addition funnel via syringe and dripped in over 15 min. The temperature was raised to 70 °C and the mixture solidified after approximately 30 min. Stirring was turned off and the reaction was heated for 3 h. After cooling to room temperature, 320 mL DI H_2O was added in portions to dissolve the solid, followed by 45.2 g KOH (80.5 mmol, 3.5 equiv. considering 85% KOH purity). Ethanol was completely removed via azeotropic distillation and the hydrolysis refluxed overnight. After cooling, the aqueous layer was acidified to pH 1-2 with concentrated HCl and extracted with ethyl acetate (4 x 250 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and solvent was evaporated to yield the carboxylic acid. The isolated carboxylic acid was decarboxylated by heating to 185 °C under reflux until CO_2 evolution ceased (approx. 2 h), with distillation of acetic acid byproduct and residual solvents. The temperature was raised to 205 °C for 5 min before distilling under vacuum to yield 55% 4,5-T6GBL over 3 steps. Vacuum distillation from CaH_2 (b.p. 62-65 °C at 75 mTorr) was performed to yield polymerization-grade monomer (Figure S1).

General Polymerization Procedures

Polymerizations were performed inside a nitrogen-filled glovebox at ambient temperature unless otherwise noted. In a typical polymerization, catalysts were measured directly into a 5 mL glass vial equipped with a micro stir bar, followed by the monomer. This mixture was stirred until homogenous and the polymerization was initiated by addition of benzyl alcohol (BnOH) via auto pipettor (for the initial (T)U screening) or a glass syringe (for all other runs). For polymerizations employing KOMe, a stock solution of (T)U and KOMe was prepared; for neat conditions, solvent was removed from the stock solution aliquot *in vacuo* before monomer was added. For the run performed in air (Table S2, run 1-AIR), all reagents were measured outside the glovebox. Aliquots were taken at given time *t* from the reaction and quenched with benzoic acid (~5 mg) in 0.6 ml $CDCl_3$ to determine conversion by ^1H NMR. After a desired time period, the polymerization was quenched by the addition of excess benzoic acid (~25 mg) in $CHCl_3$ (~3 mL). After agitation, the dissolved polymer was precipitated into cold methanol (50 mL for 2 mmol scale polymerizations) and allowed to settle for 24 h before filtration and washing with cold MeOH. Polymers were dried in a vacuum oven at 50-60 °C for 24 h; samples used for thermal analysis and depolymerization experiments were further purified by dissolving in $CHCl_3$ and re-precipitating into cold MeOH, followed by filtration and drying in the vacuum oven at 60 °C for 24 h.

Polymerization of 4,5-T6GBL with (T)U/Base/ROH (Table 2, Entry 1)

To a 5 mL vial containing a stir bar was added 3.9 mg DiiPrTU (0.05 mmol) and 7.4 mg IMes (0.05 mmol), followed by 0.272 g (1.94 mmol) monomer. The mixture was stirred until homogeneous (5-10 min), then 1.0 µl (9.7 µmol) BnOH was injected to initiate the polymerization.

Polymerization of 4,5-T6GBL with TU/KOMe (Table 3, Entry 1)

A stock solution was made with 10.0 mg (0.143 mmol) KOMe, 68.6 mg (0.428 mmol) DiiPrTU and 1.0 mL THF. To a separate vial equipped with a stir bar and Teflon-lined cap, 0.280 g (2.0 mmol) 4,5-T6GBL was added. To stirred monomer was added 140 µL stock solution to initiate the polymerization.

Polymerization of 4,5-T6GBL with NHC (Table 4, Entry 2)

To a 5 mL vial containing a stir bar was added 7.2 mg (0.04 mmol) $I^{t}Bu$, followed by 280.4 mg (2.00 mmol) 4,5-T6GBL. The reaction stirred until gelation and was quenched after 24 h.

Synthesis of Block Copolymer

To a 5 mL vial containing a stir bar was added 7.8 mg TU-3, 14.8 mg IMes, 0.272 g 4,5-T6GBL, and 145 µL THF. After all solids were dissolved, the polymerization was initiated by injection of 1.0 µL BnOH. After 4 h, an aliquot was removed for NMR and GPC analysis. A solution of 0.280 g lactide in 500 µL THF was added with vigorous stirring and quenched after 10 min.

Depolymerization Procedure

Inside the N_2-filled glovebox, a 10 mL thick-walled pressure reactor was loaded with 55 mg polymer sample and aliquot (1 mL) of catalyst in toluene (10.9 mg/mL). The sealed reactor was removed from the glovebox and heated at 120 °C for 24 h. The reactor was cooled slightly before being opened and quenched with benzoic acid while hot. When monitored for conversion over time, 100 mg polymer sample and a pressure vessel equipped with a sidearm were used.

Absolute Molecular Weight Measurements

Polymer absolute weight-average molecular weight (M_w), number-average molecular weight (M_n), and dispersity indices ($Đ = M_w/M_n$) were measured via gel-permeation chromatography (GPC). The GPC instrument consisted of an Agilent HPLC system equipped with one guard column and two PLgel 5 μm mixed-C gel permeation columns, coupled with Wyatt DAWN HELEOS II multi (18)-angle light scattering and Wyatt Optilab TrEX dRI detectors. The analysis was performed at 40 °C using chloroform as the eluent at a flow rate of 1.0 mL/min, using Wyatt ASTRA 7.1.2 molecular weight characterization software. The refractive index increments (d*n*/d*c*) of the linear and cyclic P(4,5-T6GBL) used were 0.0706 ± 0.0004 mL/g and 0.0718 ± 0.0014 mL/g, respectively, determined in a previous study.[4] The AB block copolymer was analyzed by exact concentration in place of a d*n*/d*c* value.

Spectroscopic Characterizations

Low M_n samples were analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI–TOF MS). An Ultraflex MALDI-TOF mass spectrometer (Bruker Daltonics) was operated in positive ion, reflector mode using a Nd:YAG laser at 355 nm and 25 kV accelerating voltage. A thin layer of a 1% NaI solution was first deposited on the target plate, followed by a mixture of 10 μl sample and matrix (dithranol, 20mg/mL in MeOH, 10% AAC). External calibration was done using a peptide calibration mixture (4 to 6 peptides) on the same sample plate. The raw data was processed using mMass software.

NMR spectra were recorded on a Bruker 400 MHz (FT 400 MHz, ^{1}H; 100 MHz, ^{13}C). Chemical shifts were referenced to internal solvent resonances and reported as parts per million relative to $SiMe_4$.

Thermal Analysis

Decomposition onset temperatures (T_d) and maximum rate decomposition temperatures (T_{max}) of the polymers were measured by thermal gravimetric analysis (TGA) on a Q50TGA Analyzer, TA Instrument. Polymer samples were heated from room temperatures to 700 °C at a heating rate of 10 °C/min. Values of T_{max} were obtained from derivative (wt %/°C) vs. temperature (°C) plots and defined by the peak maximum, while T_d values were obtained from wt% vs. temperature (°C) plots and defined by the temperature of 5% weight loss. The glass-transition temperature (T_g) of purified and thoroughly dried polymer samples were measured by differential scanning calorimetry (DSC) on an Auto Q20, TA Instrument. All T_g values were obtained from a second scan (10 °C/min) after the thermal history was removed by the first scan (10 °C/min).

Table S1 Enthalpy (ΔH_p°) and entropy (ΔS_p°) of polymerization for various lactone monomers[5-7]

Monomer	Ring Size	ΔH_p^0 (kJ mol^{-1})	ΔS_p^0 (J mol^{-1} K^{-1})
β-propiolactone	4	-75	-55
γ-butyrolactone	5	-5.4	-40
3,4-T6GBL	5+6	-20	-75
4,5-T6GBL	5+6	-18	-65
δ-valerolactone	6	-27	-65
L-Lactide	6	-29	-41
ε-caprolactone	7	-14	-10

Table S2 Detailed results of initial (T)U/organic base screening

Entry	Catalyst(s)	Time (h) (gel)	Conv. (%)[a]	$M_{\text{n, GPC}}$ (kg/mol)[b]	$M_{\text{n, theor}}$ (kg/mol)[c]	Đ (M_w/M_n)[b]
1	TU-3/IMes	(1 min) 24	(53) 83	10.8	11.7	1.11
1-AIR-A	TU-3/IMes	(5 min) 6.5	(53) 76	11.7	10.7	1.07
1-AIR-B	TU-3/IMes	(5 min) 7	(51) 78	11.2	11.0	1.05
2	TU-3/BEMP	(18) 40	(60) 70	8.22	9.92	1.04
3	TU-3/DBU	110	6	-	-	-
4	U-3/ IMes	(1 min) 24	(63) 81	9.50	11.5	1.12
5	U-3/ BEMP	(2) 24	(75) 82	10.1	11.6	1.09
6	U-3/ DBU	96	20	3.56	2.91	1.40
7	TU-2/IMes	(24) 48	(57) 67	9.06	9.50	1.08
8	TU-2/BEMP	(48) 72	(58) 61	7.70	8.66	1.04
9	TU-2/DBU	110	13	-	-	-
10	U-2/IMes	(3) 24	(50) 80	10.2	11.3	1.11
11	U-2/BEMP	(3.5) 24	(69) 81	9.74	11.5	1.10
12	U-2/DBU	(24) 48	(53) 68	7.08	9.64	1.08
13	U-1/IMes	(24) 72	(42) 65	5.88	9.22	1.08
14	U-1/BEMP	(24) 72	(46) 69	7.45	9.78	1.07
15	U-1/DBU	(24) 72	(55) 73	8.14	10.3	1.08
16	TU-1/IMes	96	8	-	-	-
17	TU-1/BEMP	96	6	-	-	-
18	TU-1/DBU	96	14	-	-	-

All polymerizations performed inside N_2-filled glovebox (except 1-AIR) at room temperature with 2 mmol monomer, no solvent and [M]/[(T)U]/[Base]/[I] = 100/2.5/2.5/1; I = BnOH. [a] Monomer conversion determined by ^{1}H NMR in $CDCl_3$. [b] M_n and Đ values determined by GPC at 40 °C in $CHCl_3$. [c] Calculated based on: $([M]_0/[I]_{0)}$ × Conv.% × (molecular weight of 4,5-T6GBL) + (molecular weight of I).

Table S3 Controls without (T)U

Entry	Base	[M]/[B]/[I]	Time (h)	Conv. (%)[a]
1	IMes	100/2.5/1	96	20%
2	BEMP	100/2.5/1	96	0%
3	DBU	100/2.5/1	96	0%

All polymerizations performed inside N_2-filled glovebox at room temperature with 2 mmol monomer, no solvent, and I = BnOH.
[a] Monomer conversion determined by ^{1}H NMR in $CDCl_3$

Table S4 Higher DP trials with U-3/IMes

Entry	[M]/[U-3]/[IMes]/[I]	Time (h) (gel)	Conv. (%)[a]	$M_{n,\text{GPC}}$ (kg/mol)[b]	$M_{n,\text{theor}}$ (kg/mol)[c]	$Đ$ (M_w/M_n)[b]	I^* (%)[d]
1	200/1/1/1	(1 h) 24	(47) 71	8.93	19.9	1.06	223
2	200/2.5/2.5/1	(7 min) 24	(55) 83	13.0	23.4	1.11	180
3	200/5/5/1	(0 min) 24	(58) 88	13.8	25.3	1.18	183
4	500/2.5/2.5/1	(20 min) 24	(41) 71	19.0	50.7	1.07	267

All polymerizations performed inside N_2-filled glovebox at room temperature with 2 mmol monomer, no solvent and I = BnOH.
[a] Monomer conversion determined by ^{1}H NMR in $CDCl_3$. [b] M_n and $Đ$ values determined by GPC at 40 °C in $CHCl_3$. [c] Calculated based on: $([M]_0/[I]_{0)}$ × Conv.% × (molecular weight of 4,5-T6GBL) + (molecular weight of I), using exact equivalents of monomer measured. [d] $I^* = (M_{n,\text{theor}} / M_{n,\text{GPC}}) \times 100$

Table S5 Organocatalytic depolymerization of P(4,5-T6GBL)

Run	Catalyst	Cat. Loading (mol%)	Solvent	Temp. (°C)	Time (h)	Conv.(%)[a]
1	I^{t}Bu	2	Tol 0.4M	120	24	0
2	TU-3/IMes	2	Tol 0.4M	120	24	8
3	TBD	2	Tol 0.4M	120	24	100
4	TBD	2	THF 0.4M	80	24	50
5	TBD	1	Tol 1.0M	120	10	96

[a] Polymer conversion determined by ^{1}H NMR in $CDCl_3$.

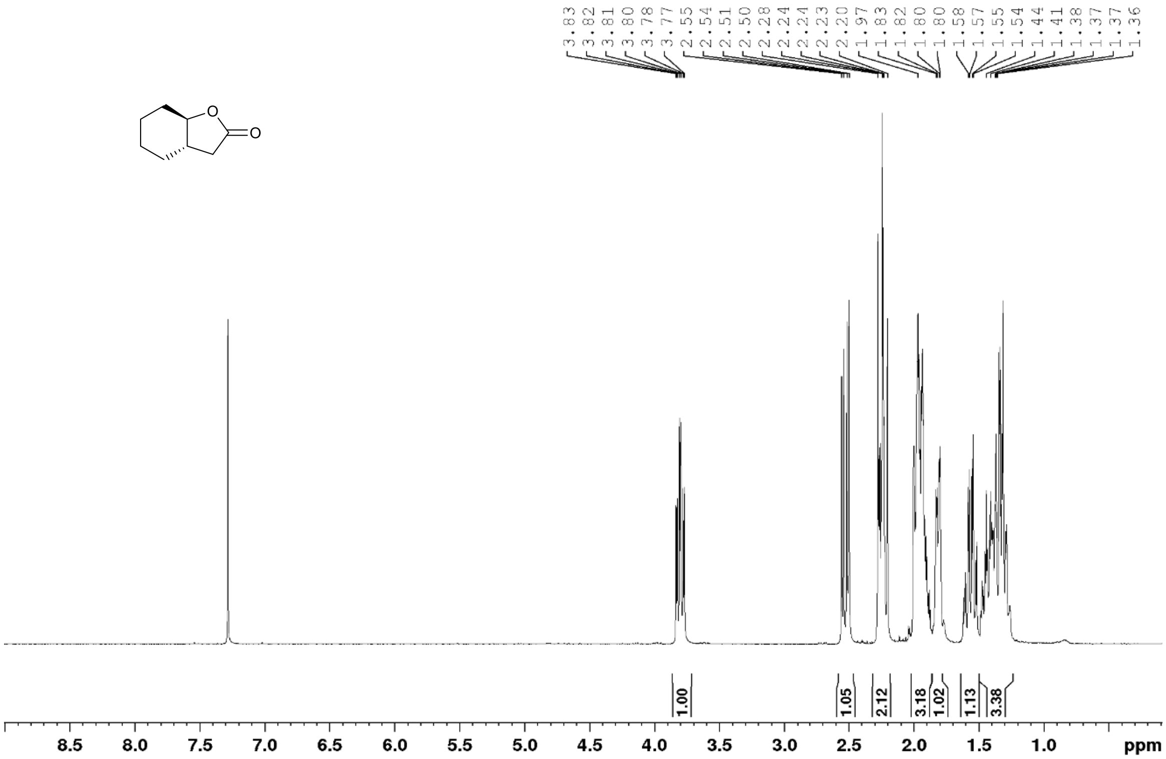

Figure S1 ^{1}H NMR (CDCl$_3$, 25 °C) spectrum of 4,5-T6GBL.

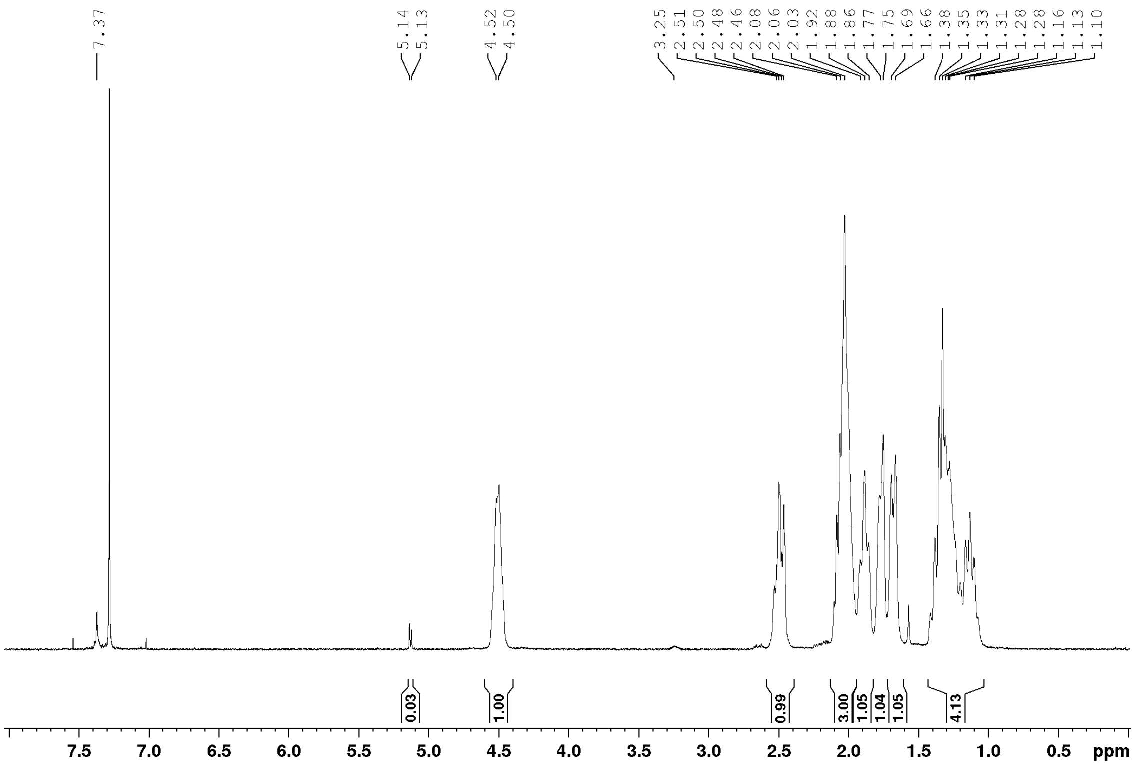

Figure S2 ^{1}H NMR (CDCl$_3$, 25 °C) spectrum of linear P(4,5-T6GBL) obtained by [M]/[U-3]/[IMes]/[BnOH] = 100/2.5/2.5/1.

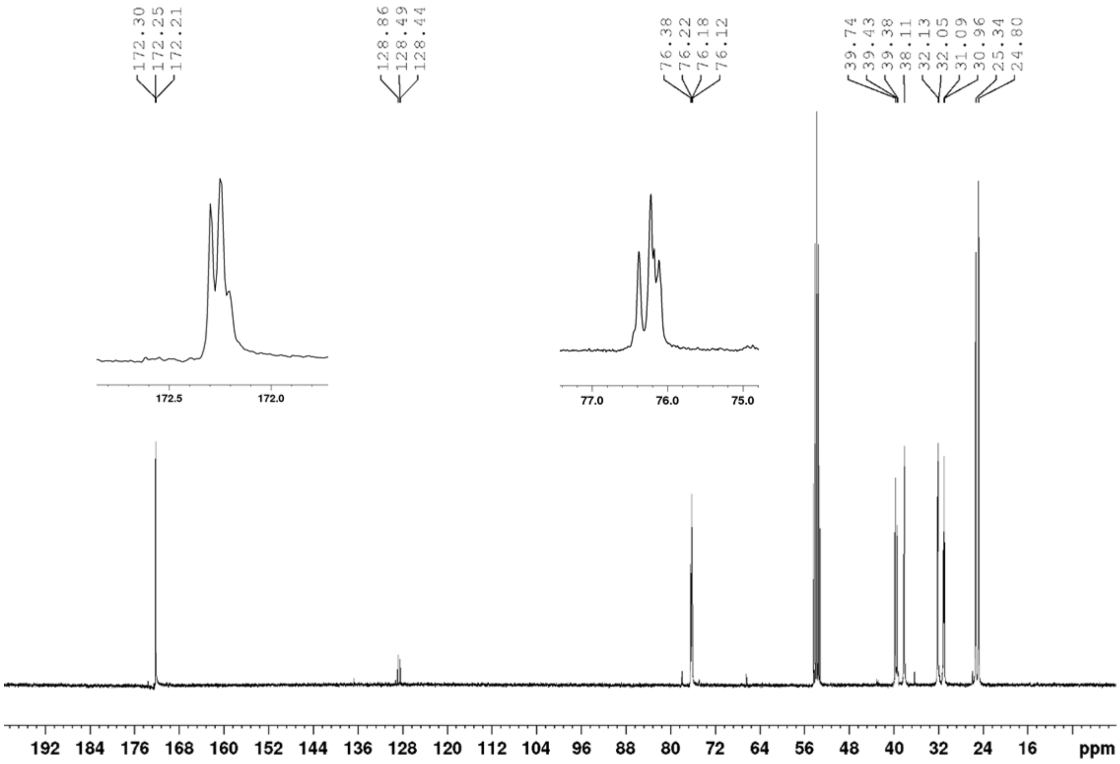

Figure S3 ^{13}C NMR (CD_2Cl_2, 25 °C) spectrum of linear P(4,5-T6GBL) obtained by [M]/[U-3]/[IMes]/[BnOH] = 100/2.5/2.5/1.

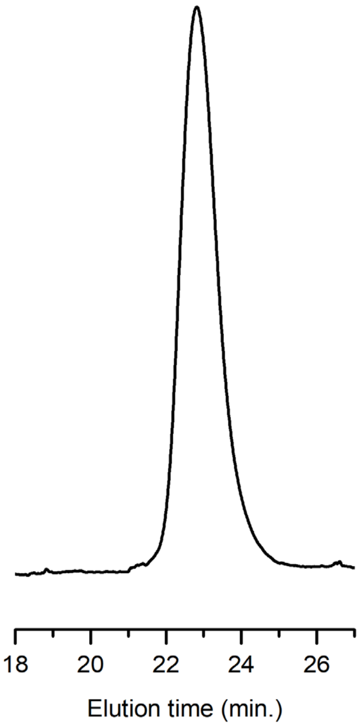

Figure S4 GPC trace of linear P(4,5-T6GBL) prepared by [M]/[U-3]/[IMes]/[BnOH] = 100/2.5/2.5/1, M_n = 10.1 kDa, $Đ$ = 1.09.

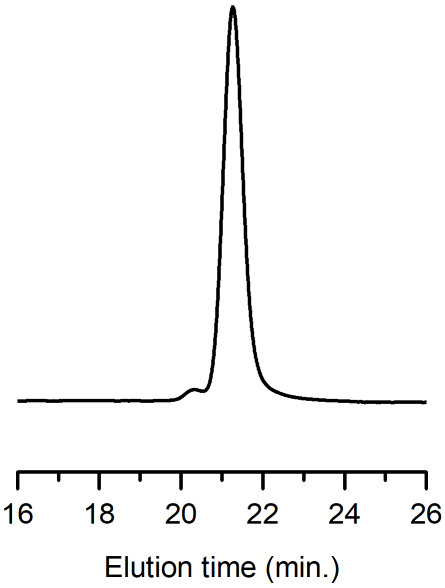

Figure S5 GPC trace of linear P(4,5-T6GBL) prepared by [M]/[TU-3]/[IMes]/[BnOH] = 500/5/5/1, M_n = 39.5 kDa, $Đ$ = 1.03.

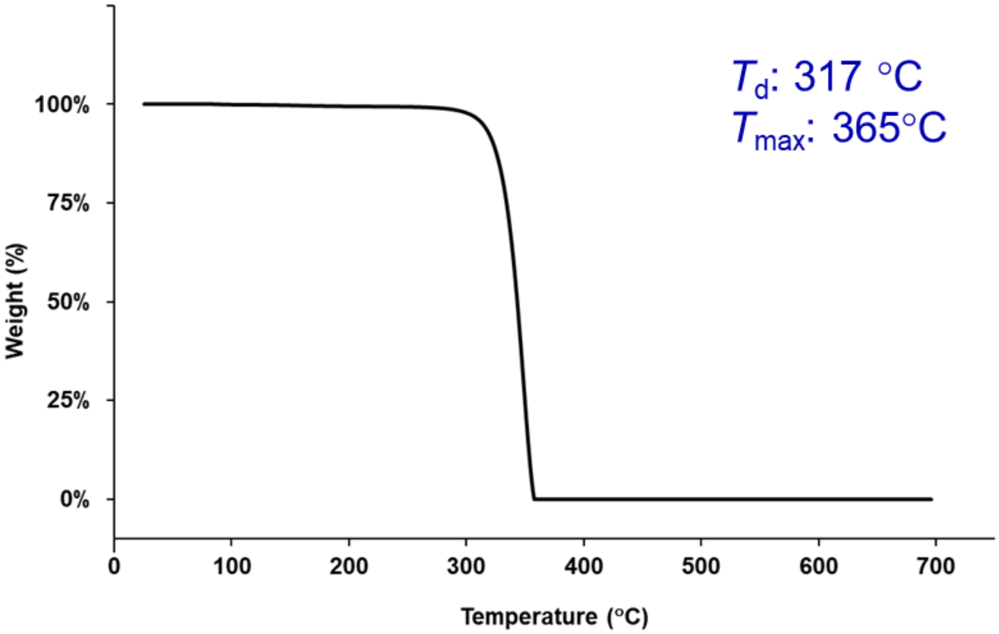

Figure S6 TGA curve of P(4,5-T6GBL) obtained by [M]/[TU-3]/[IMes]/[Ph_2CHCH_2OH] = 200/5/5/1, M_n = 21.5 kDa, $Đ$ = 1.03.

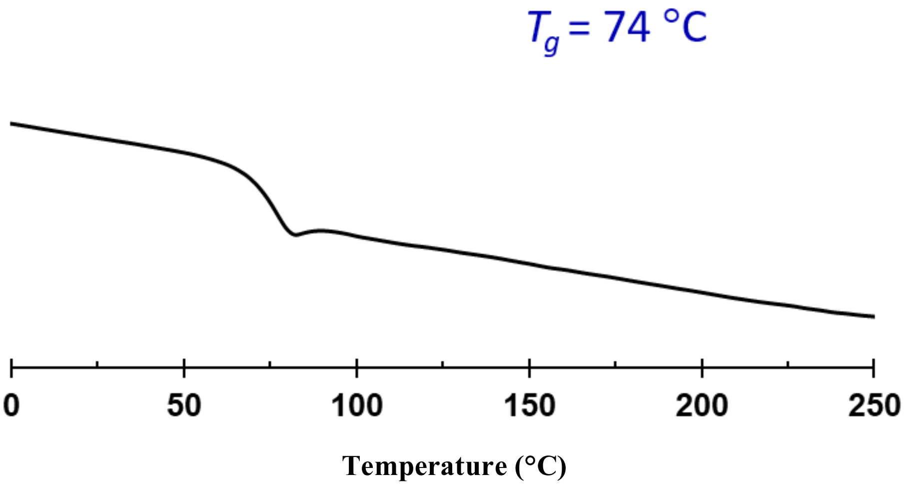

Figure S7 DSC curve of P(4,5-T6GBL) obtained by [M]/[TU-3]/[KOMe] = 250/3/1, M_n = 90 kDa, $Đ$ = 1.07.

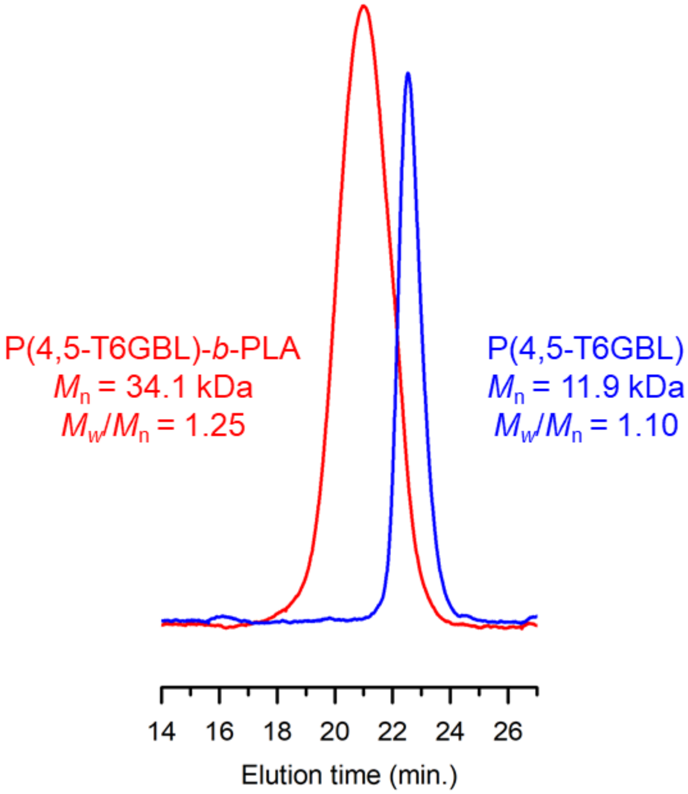

Figure S8 GPC traces of linear P(4,5-T6GBL) before and after chain extension via block copolymerization.

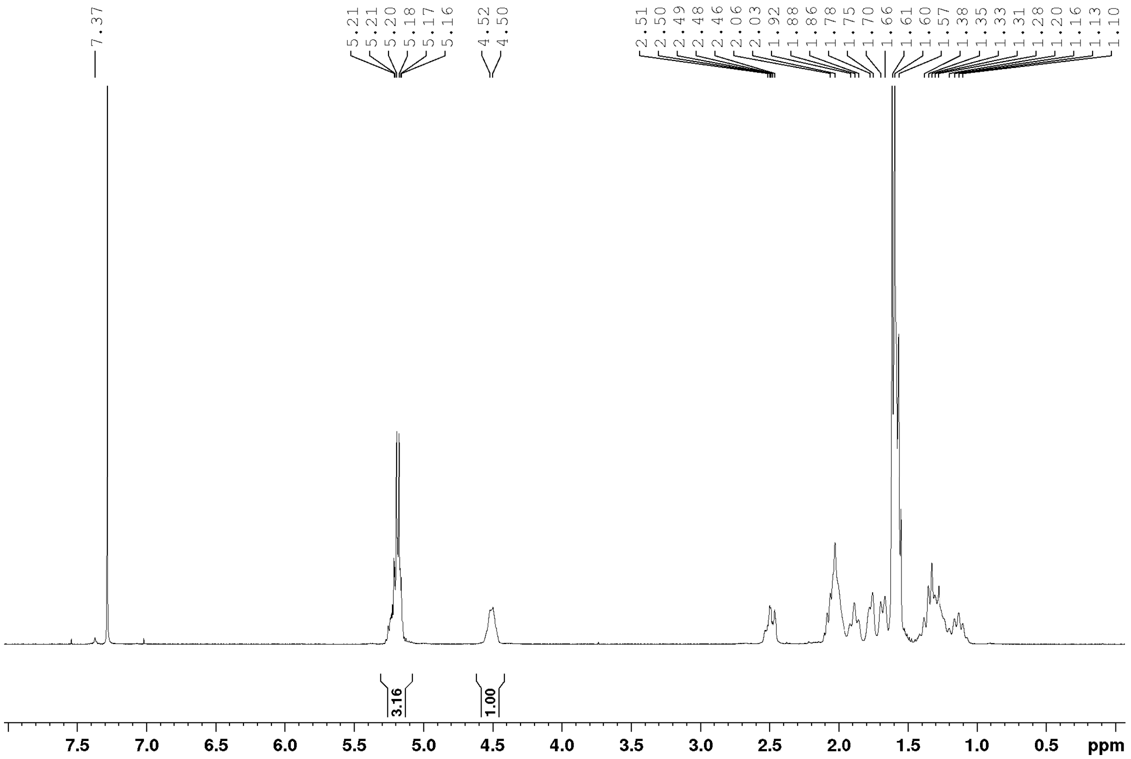

Figure S9 ^{1}H NMR (CD_2Cl_2, 25 °C) spectrum of isolated P(4,5-T6GBL)-*co*-PLA.

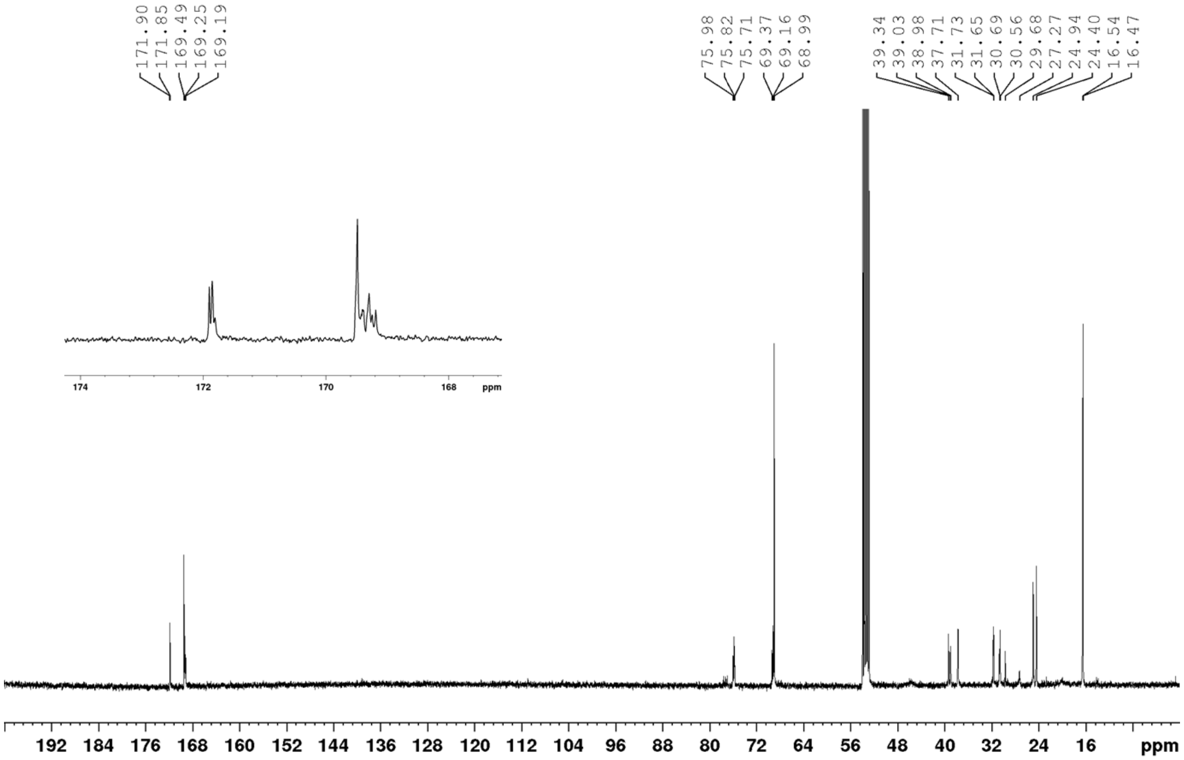

Figure S10 ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of isolated P(4,5-T6GBL)-*co*-PLA.

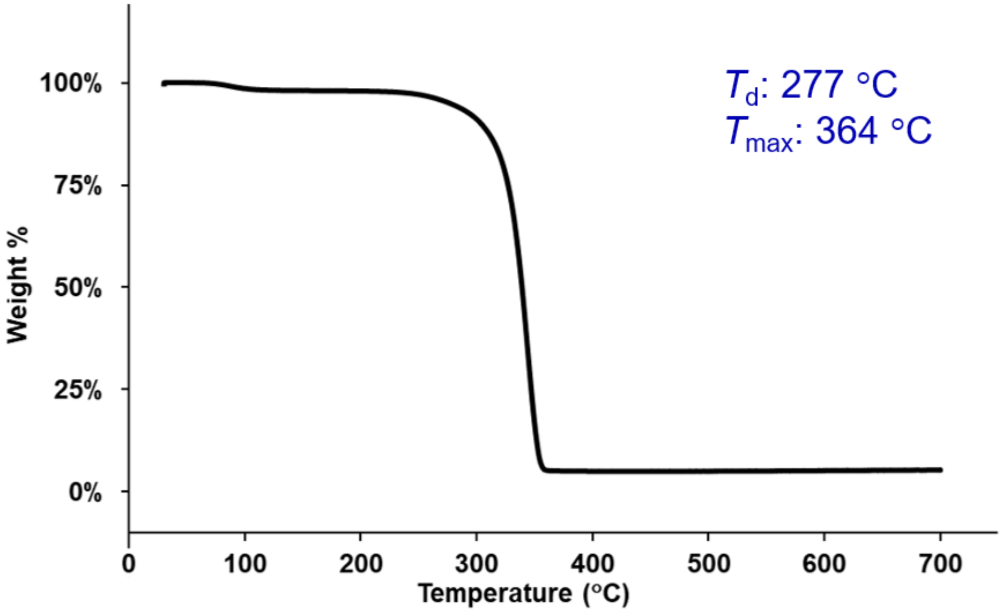

Figure S11 TGA curve of P(4,5-T6GBL)-*co*-PLA, M_n = 34.1 kDa, $Đ$ = 1.25.

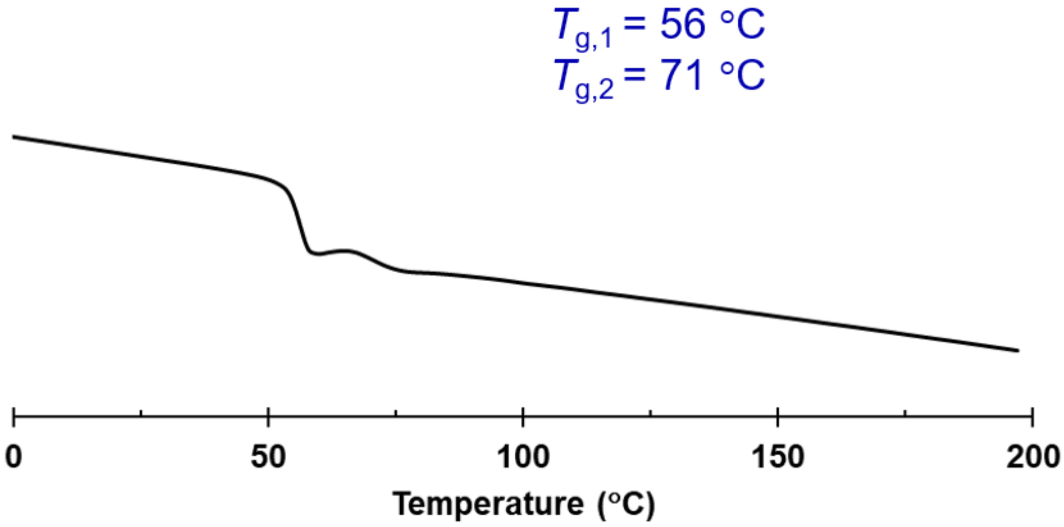

Figure S12 DSC curve of P(4,5-T6GBL)-*co*-P(LA).

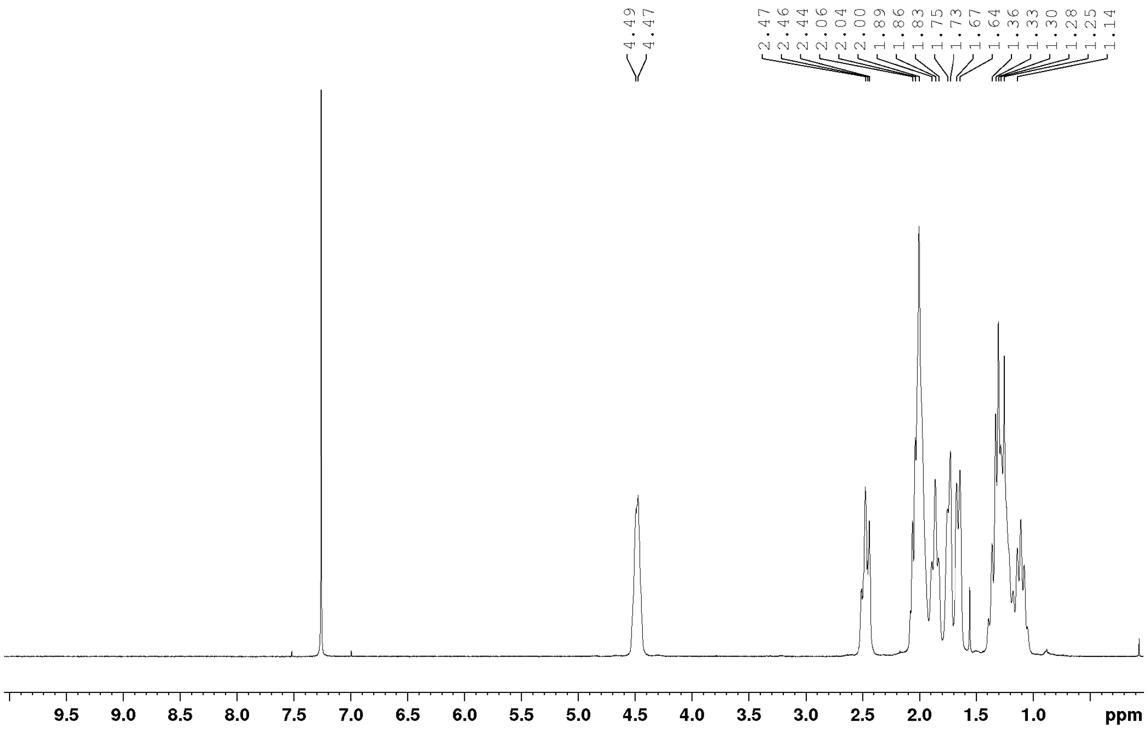

Figure S13 ^{1}H NMR (CDCl$_3$, 25 °C) spectrum of cyclic P(4,5-T6GBL) obtained by [M]/[I^{t}Bu] = 100/1.

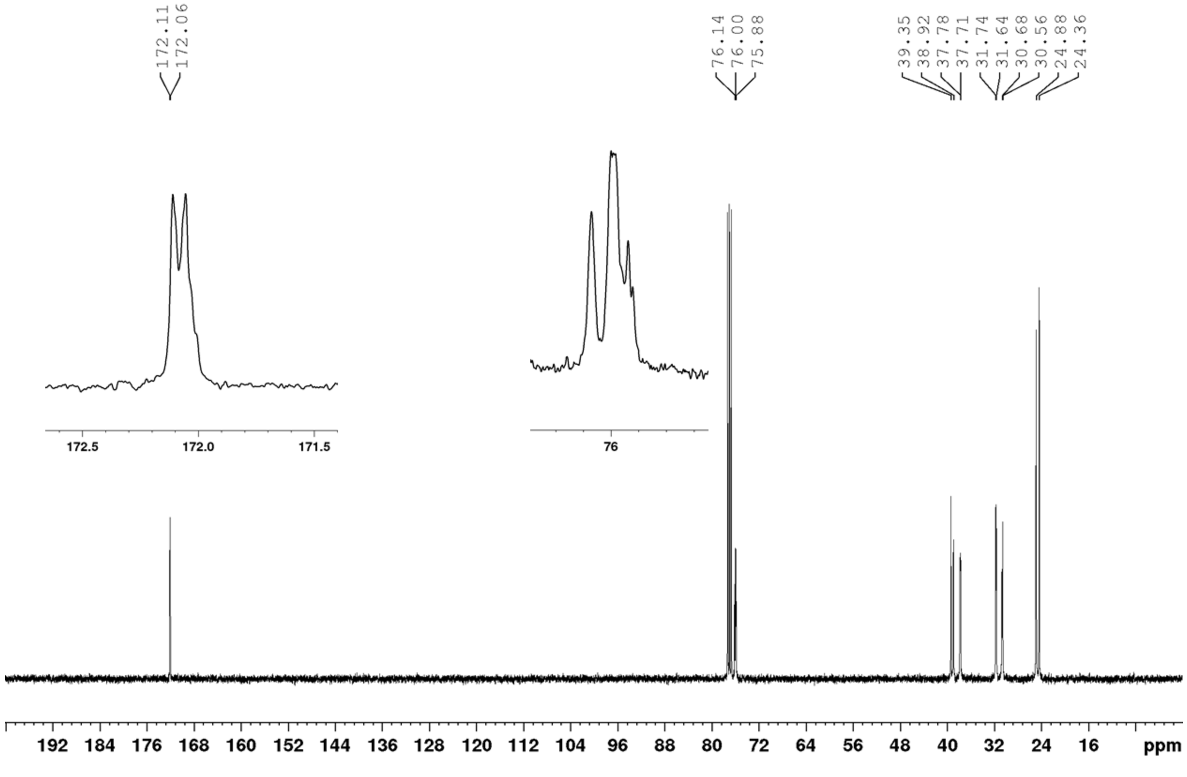

Figure S14 ^{13}C NMR (CDCl$_3$, 25 °C) spectrum of cyclic P(4,5-T6GBL) obtained by [M]/[I^{t}Bu] = 100/1.

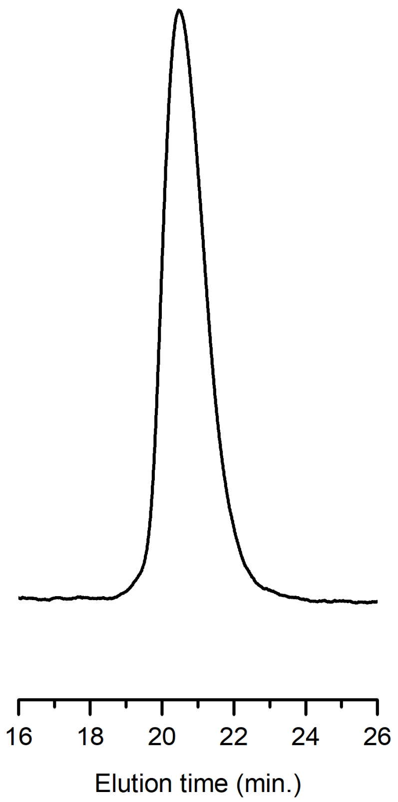

Figure S15 GPC trace of cyclic P(4,5-T6GBL) obtained by [M]/[I^{t}Bu] = 100/1, M_n = 40.6 kDa, $Đ$ = 1.21.

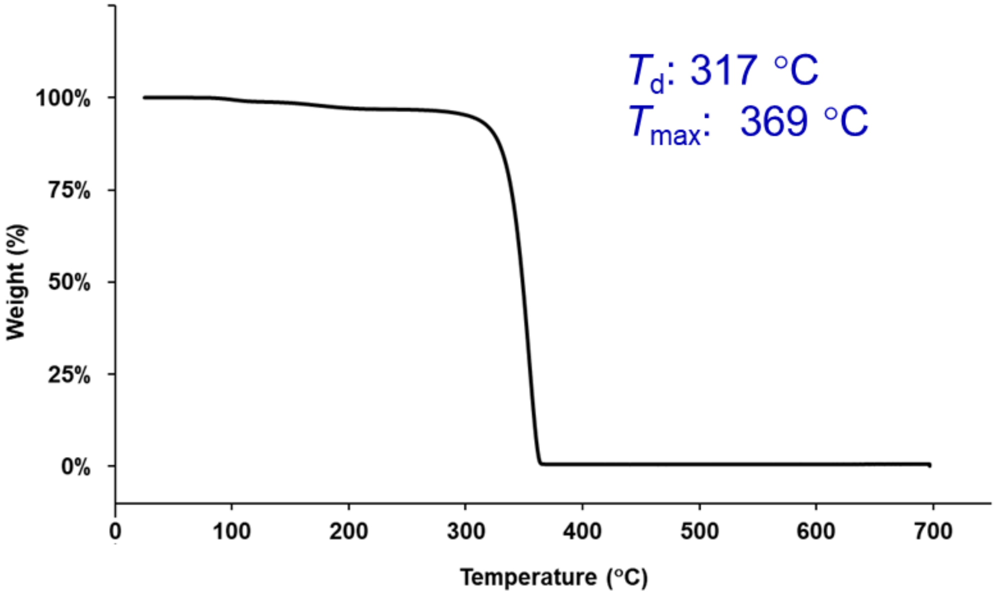

Figure S16 TGA curve of cyclic P(4,5-T6GBL) obtained by [M]/[I^{t}Bu] = 100/1, M_n = 40.6 kDa, $Đ$ = 1.21.

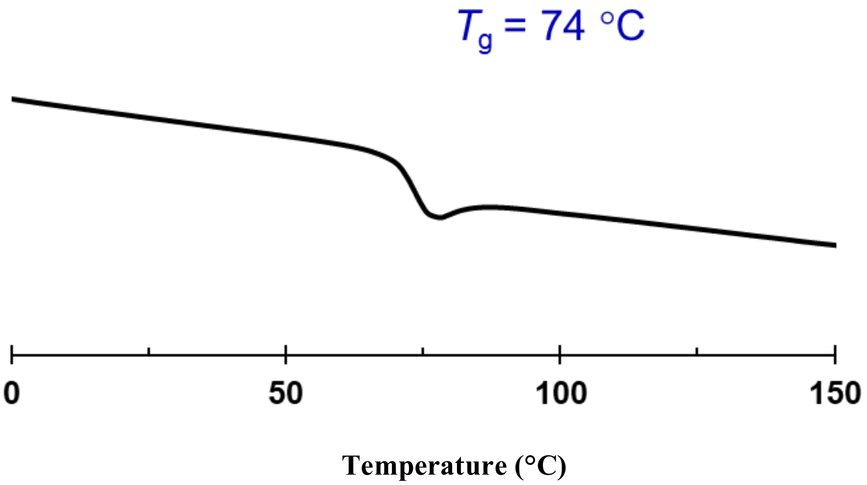

Figure S17 DSC curve of cyclic P(4,5-T6GBL) obtained by [M]/[I^{t}Bu] = 100/1.

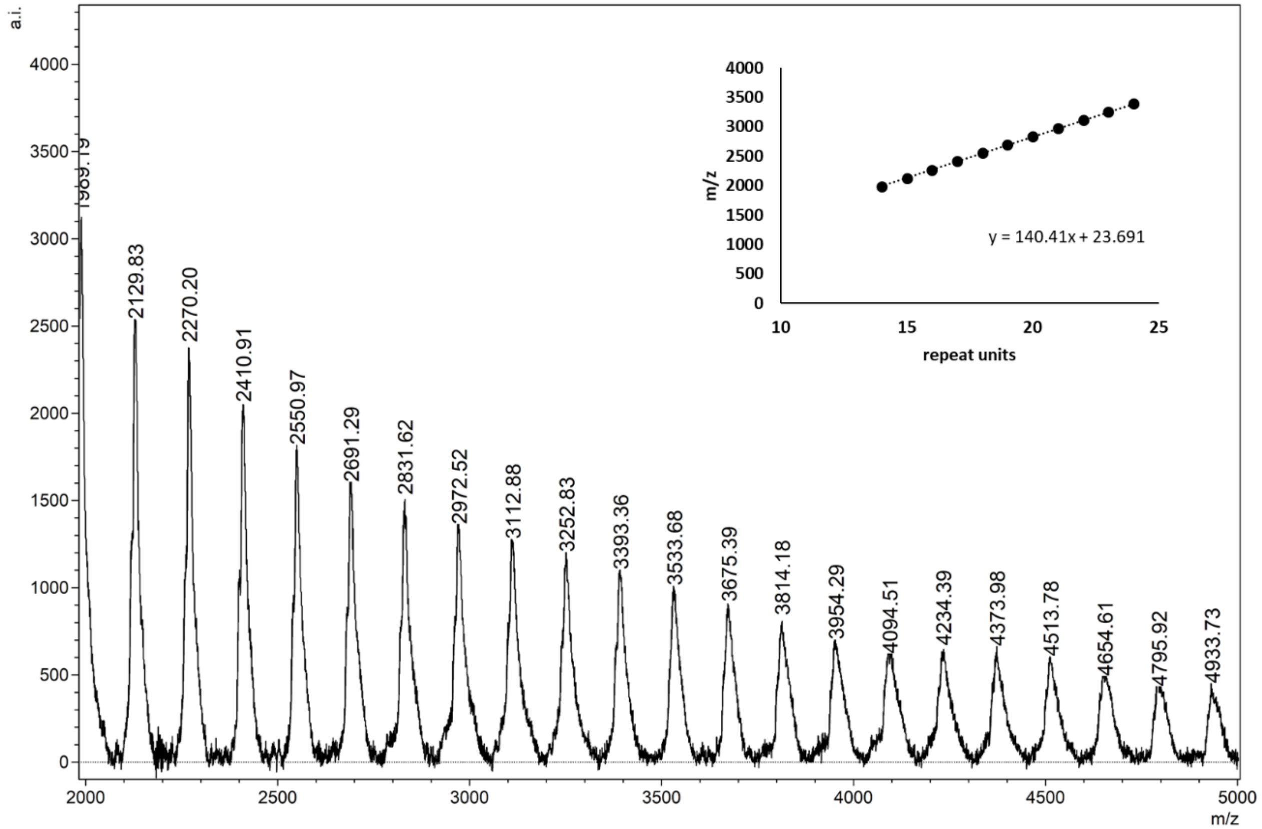

Figure S18 MALDI-TOF spectrum cyclic P(4,5-T6GBL) obtained by [M]/[I^{t}Bu] = 100/1.

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